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Suspended electrodialytic remediation for detoxification of copper-mine tailings

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Abstract

A major environmental effect of mining activities origin from the production of tailings, and the exposure of these to ambient physical and chemical conditions. In modern mining, and in particular when mining in the pristine and vulnerable Arctic environment, special precautions should be made. In this regard, special attentions should be paid to tailings handling and tailings deposition. One method in development for detoxification of tailings is electrokinetic (EK) or electrodialytic (ED) extraction of left toxic elements. Six electrodialytic experiments in laboratory scale show that it is possible to extract residual Cu from Cu mine tailings by electrodialysis in suspension independently of tailings age. Cu can be separated from other extracted elements because it is precipitated as metallic Cu directly at the cathode. From these small scale laboratory experiments a maximum energy consumption for the electrodialysis process can be calculated to < 80kWh/ton to remove half of the copper.

1. Introduction

A major environmental effect of mining activities origin from the production of tailings, and the exposure of these to ambient physical and chemical conditions. In modern mining, and in particular when mining in the pristine and vulnerable Arctic environment, special precautions should be made. In this regard, special attentions should be paid to tailings handling and tailings deposition. One method in development for detoxification of tailings is electrokinetic (EK) or electrodialytic (ED) extraction of left toxic elements.

Experimental results have shown that application of a direct current field (EK) over tailings can be used to remove Cd, Cu, Pb, and Zn from tailings soils (Kim et al., 2002; Kim and Kim, 2001); As from tailings (Baek et al., 2009; Isosaari and Sillanpää, 2012); and Cu from tailings (Hansen et al., 2013; Hansen and Rojo, 2007).

It has been shown that the efficiency increases when ion-exchange membranes are placed as barriers between electrodes and tailings (ED) for removal of Cu from Cu mine tailings. Still, however, a major concern is the long treatment-time required for element-transport through the tailings matrix. Therefore several enhancement methods have been investigated to decrease treatment time. Improvements were obtained for removal of Cu from Cu mine tailings by: pre-treatment of tailings with acid (sulphuric or citric acid) (Hansen et al., 2007a; Rojo et al., 2006); insertion of bipolar electrodes to accumulate Cu (Hansen et al., 2007b); and implementation of pulsed electric fields (Hansen and Rojo, 2007) or sinusoidal field (Rojo et al., 2010; Rojo et al., 2012). It was also shown that the energy-consumption for treatment of arsenic tailings (but not treatment time) could be reduced by combination of electrokinetic treatment and anaerobic bioleaching (Lee et al., 2009).

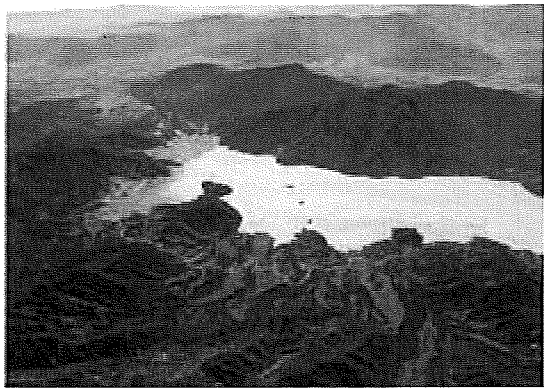

Figure 1: The Caren tailings impoundment at the Codelco-El Teniente Cu mine in Chile.

When comparing treatment of fresh (< 2 years old) and aged (>20 years old) tailings, it was observed that although removal of Cu from fresh tailings improved significantly by pre-treatment with acid, removal from aged tailings was even more efficient – without acid pre-treatment. This is due to the natural acidification occurring by oxidation of sulphide minerals during the aging process (Hansen et al., 2007a; Hansen et al., 2013).

It was shown for other materials such as ashes and sludge that electrodialytic treatment time can be significantly reduced by treatment in a homogenously stirred suspension, as opposed to a solid matrix (Ottosen et al., 2012). The main effect is thought to be the reduced transport distance between the material to be treated, and the electrode compartments. However energy and time may also be saved by the avoided build up of polarization phenomena, which are also the phenomena approached when applying pulsed current and sinusoidal current fields (Hansen and Rojo, 2007; Rojo et al., 2010; Rojo et al., 2012). As fresh tailings leave the mine in a liquid suspension, it may be feasible to treat those directly as such prior to deposition, and even consider the treatment as a final extraction step in the mineral extraction process. In addition, as mineral prices increase, re-mining of old tailings deposits become increasingly common. For this purpose, electrodialytic treatment of old tailings in suspension may also be a potential technological alternative. It was shown that Cu can be removed from fresh tailings by electrodialytic treatment in suspension, when suspended in sulphuric acid, and that the rate of removal increases with degree of suspension (Hansen et al., 2008). Works on other materials, however showed that when treating by electrodialysis in suspension, acid addition impedes remediation as opposed to when treating by electrodialysis in a static matrix (Jensen et al., 2007a; Nystroem et al., 2006).

The aim of this work is to further evaluate the potential of treating suspended Cu mine tailings by electrodialysis. Comparison of treatment at two different current densities with Cu mine tailings of three different ages suspended in water is the focus.

2. Materials and methods

2.1 Tailings characteristics

The mine tailings used were all from the Codelco-El Teniente Cu mine in VI Region in Chile. Three different tailings of different age were used.

a) Canal: freshly processed tailings from the ore concentrator, sampled directly from the tailings waste canal, which feeds the impoundments.
b) Caren: 5-10 years old tailings from the Caren impoundment.
c) Cauquene: 20-30 year old tailings from the Tranque Cauquene impoundment.

Figure 1 shows the Caren impoundment. Mineralogical characteristics of the fresh tailings are described in (Hansen et al., 2005).

2.2 Electrodialysis experiments

Electrodialysis experiments were made in cylindrical Plexiglas-cells with three compartments. Compartment II, which contained the tailings-slurry, was 5 cm long and 8 cm in inner diameter. The setup is visualized in *figures 2 and 3*.

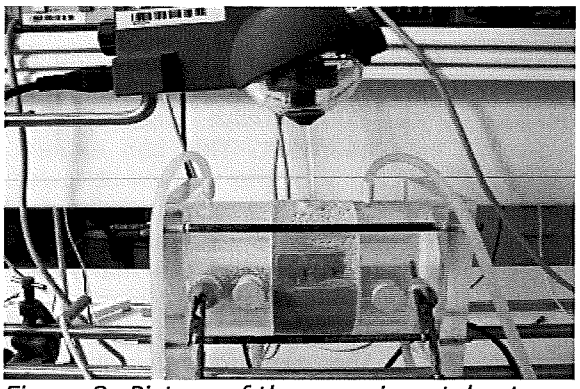

Figure 2: Picture of the experimental setup.

The slurry was kept in suspension by constant stirring with plastic-flaps attached to a glass-stick and connected to an overhead stirrer. The anolyte was separated from the soil specimen by an anion-exchange membrane, and the catholyte was separated from the soil specimen by a cation-exchange membrane (AR204SZRA and CR67 HVY HMR427 respectively.

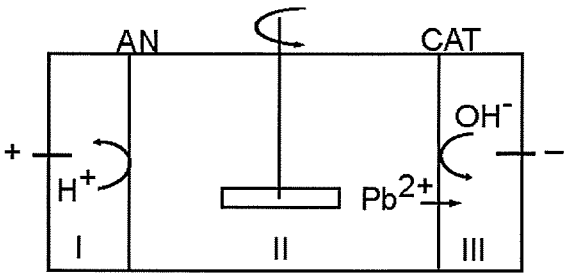

Figure 3: Schematic view of a cell used for experimental remediation of tailings in suspension. AN = anion-exchange membrane, CAT = cation-exchange membrane. I = anolyte compartment, II = compartment containing sediment slurry, III = catholyte compartment.

Platinum coated titanium electrodes were used as working electrodes. The catholyte and the anolyte initially consisted of 0.01M $NaNO_3$ adjusted to pH 2 with HNO_3. pH in the catholyte was kept between 1 and 2 by manual addition of HNO_3 (7M). The liquid to solid ratio (L/S) was 4 (25g air-dried tailings and 100 mL distilled water). All experiments lasted for one week. An overview of the experimental variables (material, suspension liquid and current density) is given in *table 1*.

Table 1: Electrodialytic experiments

Experiment	Material	Current (mA/cm^2)
Fresh 0.1	Canal	0.1
Mid 0.1	Caren	0.1
Aged 0.1	Cauquenes	0.1
Fresh 0.2	Canal	0.2
Mid 0.2	Caren	0.2
Aged 0.2	Cauquenes	0.2

After the closure of the experiments, electrodes were rinsed in 5M HNO_3, and membranes in 1M HNO_3. Samples of all liquids incl. electrolytes were saved for analysis of Cu. The tailings suspension was filtered through filter paper, and a sample of the filtrate saved for analysis. The wet tailings were dried at 105°C overnight and saved for analysis of Cu.

2.3 Extraction experiments

Reference extractions (*table 2*) without current application were made by shaking 5,0 g tailing material with 20,0mL DI water or 20,0 mL HNO_3 pH 4 on a shaking table for one week. The slurry was filtered and a sample of the liquid saved for analysis.

Table 2: Reference extractions without current application

Ref.	Material	Extractant
Fresh Acid	Canal	HNO_3 pH 4
Mid Acid	Caren	HNO_3 pH 4
Aged Acid	Cauquenes	HNO_3 pH 4
Fresh EDW	ED treated Canal	DI water
Mid EDW	ED treated Caren	DI water
Aged EDW	ED treated Cauquenes	DI water

2.4 Analytical methods

Cu was analyzed by flame AAS according to the Danish standard method DS259 (Dansk Standardiseringsraad, 2003) which includes acid digestion of 1g dry tailings material with 20.00mL of 7M HNO_3 in autoclave at 200kPa and 120°C for 30 minutes. The Cu-content in solution was measured by AAS after filtration through a 0.45µm filter. pH was measured on all samples by a Radiometer electrode. All analysis were made in triplicate.

Analysis of the Cu in the tailings and process liquids was made prior to and after the experimental remediation. Non-acidic liquid samples were preserved with one part of concentrated HNO_3 to four parts of liquid prior to analysis.

After experimental remediation and analysis of samples, the fraction of Cu remaining in the tailings (compartment II), dissolved in the suspension solution (compartment II), transported to the cathode (compartment III), precipitated at the cathode, and transported to the anode (compartment I) were calculated.

3. Results and discussion

The mass balances for Cu understood as mass of Cu found in the ED cell system after treatment experiment in percent of the mass of Cu calculated from initial digestion and analysis of the untreated tailings were all between 91 and 101%, which is acceptable considering the standard deviations on the analysis of Cu (*table 3*). pH decreased during treatment from natural to just below 2 due to the acid produced in the ED-cell by water-splitting at the anion-exchange membrane (Nystroem et al., 2005) (*table 3*). The Cu concentration was reduced from around 1000mg/kg to around 500mg/kg in all experiments (*table 3*). No significant difference in reduction could be observed between tailings of different age in opposition to what was found when treating tailings in solid matrix (Hansen et al., 2007a; Hansen et al., 2013). Furthermore, Cu could be removed efficiently even from fresh tailings without acid pre-treatment. The removal was slightly more efficient at the lower current density compared to the higher current density. It can be seen from *figure 4* that a small amount of the Cu was found dissolved in the suspension liquid in the middle compartment of the cell in the three experiments with low current density, while no Cu was observed there at the closure of the experiments with high current density. This shows that at the high current density, the system is under pressure, and any Cu released from the tailings is immediately transported to the cathode compartment. In a system under such pressure and lack of ions to carry the current, compensation by water splitting at the cation exchange membrane can occur (Jensen et al., 2007b) with production of hydroxide ions as result. This can explain the higher efficiency of the system at lower current. However, only a slight resistance increase was observed in the experiments with high current density as the maximum voltage observed during those experiments was 3.7 independently of tailings age, while it was 2.3 in the experiments with low current density. At such low voltage drop and current density, energy consumption becomes minimal (< 80kWh/ton to remove half of the copper). Comparing with the previous work on treatment of fresh tailings in a suspended ED-system (Hansen et al., 2008), it can be seen that higher amounts of Cu were removed in this work at lower current densities and lower L/S than in the previous work where the tailings were suspended in sulphuric acid. The main reason is likely to be that when the material is suspended in acid, the conductivity increases significantly. Two consequences of this are, that when the tailings are suspended in acid: a) much current is carried by the hydrogen ions, thus higher current densities are needed to remove other ions efficiently; b) the limiting current for water splitting is increased, and less acid is produced by water splitting at the anion exchange membrane.

Table 3: pH and Cu (mg/kg ± Std. dev.) in tailings before and after ED treatment.

Experiment	pH start	pH end	Cu start	Cu end
Fresh 0.1	7.7	1.7	997±19	475±14
Mid 0.1	7.6	1.7	1059±27	435± 7
Aged 0.1	7.4	1.7	1190±13	456± 7
Fresh 0.2	7.7	1.9	997±19	506± 1
Mid 0.2	7.6	1.9	1059±27	475±11
Aged 0.2	7.4	1.7	1190±13	492±10

With no exemptions the experiment show that the Cu removed from tailings is mainly precipitated at the cathode as metallic Cu, and only small fractions are found in the liquid phases (electrolytes) (*figure 4*). This is the typical behavior for Cu (Jensen et al., 2012), and can be considered and advantage if separation of Cu from other

metals such as Zn or Pb is the aim, as most other metals will remain dissolved in the electrolyte liquids.

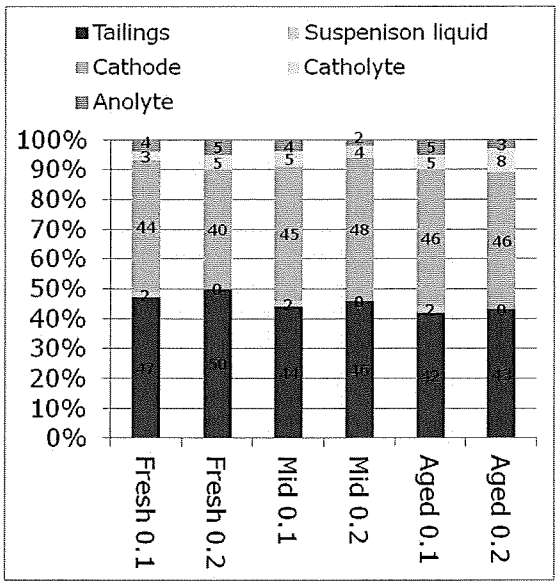

Figure 4: Results of the six electrodialysis experiments expressed as percent of the Cu found in the various compartments of the electrodialytic cell. The amount in the electrolytes include small amounts (<1%) found in the membrane material.

The reference extractions showed that independently of age of tailings, less than 1% of the Cu could be extracted from the tailings no matter with distilled water or HNO_3 at pH 4, thus the application of current significantly improved the extraction.

4. Conclusions

It is possible to extract residual Cu from Cu mine tailings by electrodialysis in suspension independently of tailings age. Faster and more energy efficient extraction is obtained when the tailings are suspended in water as opposed to acid suspension. Increasing current density to above 0.1 mA/cm^2 does not improve the extraction. Cu can be separated from other extracted elements because it is precipitated as metallic Cu directly at the cathode. From these small scale laboratory experiments a maximum energy consumption for the electrodialysis process can be calculated to < 80kWh/ton to remove half of the copper.

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